ELSEVIER

Sensors and Actuators B 24–25 (1995) 797–800

SENSORS AND ACTUATORS B CHEMICAL

Application of semiconductor gas sensor to quality control of meat freshness in food industry

Naomi Funazaki [a], Akihide Hemmi [a], Satoshi Ito [a], Yasukazu Asano [a], Yukio Yano [b] Norio Miura [c], Noboru Yamazoe [c]

[a] *DKK Corp., Kitamachi, Kichijoji, Musashino-shi, Tokyo 180, Japan*

[b] *Central Research Institute, Itohamu Foods Inc., Kubogaoka, Moriya-machi, Kitasomagun, Ibaragi 302-01, Japan*

[c] *Department of Materials Science and Technology, Kyushu University, Kasuga-shi, Fukuoka 816, Japan*

Abstract

We have investigated the possibility of utilizing a semiconductor gas sensor for quality control of meat freshness in the food industry. A semiconductor gas sensor based on In_2O_3 is exploited for detecting ethyl acetate, a typical flavour volatile component produced in the initial bacterial putrefaction of meat. Of the sensor elements examined, $Rh–La_2O_3–In_2O_3$ is found to show excellent sensitivity and selectivity to ethyl acetate at 300 °C. The sensor response signal increases with increasing meat-storage time and reflects rather well the increase of bacteria determined by a conventional colony-counting method. The multiple correlation factor between both methods is 0.8.

Keywords: Meat freshness; Semiconductor gas sensors

1. Introduction

Quality control and liability of industrial products have been gaining importance since the enforcement of ISO 9000. At present the quality control of food products relies mostly on manual analysis by experts, and a simple and easy method to replace this manual analysis is eagerly desired. Meat needs to be subjected to an aging process for attaining its optimal eating quality before being distributed to consumers. The quality control of meat is therefore totally different from the case of fish, for which being fresh with as short as possible a time lapse after catching or maintaining the pre-rigour state is important for high quality. On the other hand, meat quality is judged from the eating quality, which is optimal just before bacterial spoilage begins during the aging process. Therefore the word 'meat-freshness control' should be regarded as a complex concept involving the aging and bacterial putrefaction of meat.

Conventionally the method of counting colonies, the phase-difference microscope method, and so on, have been used to evaluate the degree of aging and bacterial putrefaction of meat. These methods are tedious and time-consuming for everyday quality control of meat freshness, but no simpler method was available until a two-line flow-injection system using enzyme sensors for putrecine and hypoxanthine was developed recently for monitoring the aging process of meat. This system is far more practical for the quality control of meat freshness than the conventional methods. However, even this system, is based on a destructive analysis of the chemical components produced in meat. It has been shown recently that the gaseous components evaporating from food can be a good measure for judging food quality. For example, a semiconductor gas sensor sensitive to a particular flavour component from consomme soup has been developed for evaluating soup quality [1,2]. The use of a gas sensor can provide a non-destructive, non-contact method of food analysis, and would be highly desirable for quality control in the food industry. On this background, we have explored the possibility of the gas-sensor-based quality control of meat freshness. As a first step of the exploration, the volatile components produced in meat under constant storage conditions were analysed as a function of storage time by means of GC–MS analysis based on a purge and trap technique [3]. As a result, ethyl acetate was found to be a typical major product at the initial stage of bacterial putrefaction. This paper deals with the development of a semiconductor gas sensor for ethyl acetate vapour as well as its applicability for

SSDI 0925-4005(94)01471-S

evaluating meat freshness at the initial stage of bacterial putrefaction.

2. Experimental

2.1. Fabrication of gas sensor

A powder of In_2O_3, SnO_2 and Fe_2O_3 was prepared from $InCl_3$, $SnCl_4$ and $Fe(NO_3)_3$, respectively, according to the technique reported previously [4,5]. La_2O_3-impregnated samples were prepared by mixing the above powder with an aqueous solution of lanthanum acetate, followed by drying in a vacuum freezer and calcining at 700 °C for 5 h. To be loaded with noble metals, each powder was impregnated with aqueous colloidal dispersions of Ru, Rh, Au and Pt (donated by Toda Kogyo Co. Ltd.) for 5 h under agitation. The loading was fixed at 0.5 wt.% for each noble metal and 5 wt.% for La_2O_3. Sensor elements of a porous thick-film type were fabricated on an aluminium substrate, on which comb-type Au electrodes (10 mm×8 mm in size), consisting of 13 Au lines lying at 0.3 mm intervals, and an internal heater (2.5 mW) were attached at the upper and back surfaces, respectively, as shown in Fig. 1.

2.2. Measurement system of sensor properties

The gas-sensing properties were tested in a conventional flow apparatus in the temperature range 200–500 °C. The sample gas containing ethyl acetate in wet air was prepared by diluting ethyl acetate cylinder gas (Nippon Sanso Co. Ltd.) with wet air and was allowed to flow over the gas sensor at a rate of 300 $cm^3\ min^{-1}$. By using the circuitry shown in Fig. 2, the electrical resistance of each element was measured in air (R_a) and in the sample gas (R_g) to evaluate the gas sensitivity (S), defined as R_a/R_g. R_a and R_g were measured in wet air of 90% relative humidity unless noted otherwise. The sensitivity values were evaluated for five sensor elements of the same type simultaneously and the mean value was taken as a representative value.

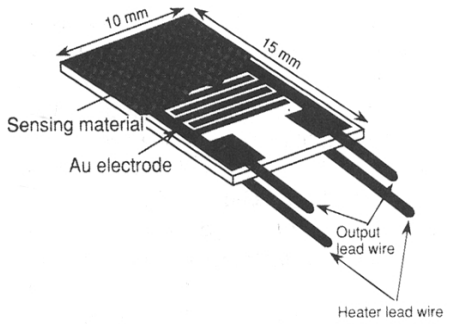

Fig. 1. Structure of gas-sensor element.

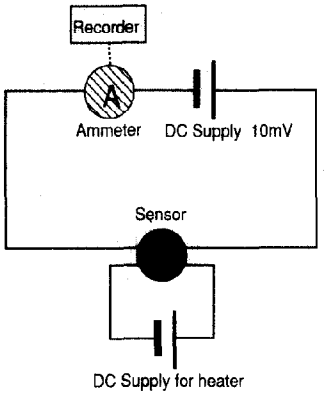

Fig. 2. Electrical circuitry used for gas-sensing experiments.

2.3. Meat sample preparation

Sirloin meat from Holstein bullocks obtained from carcasses stored for two days at 0 °C after slaughtering was cut into 20 mm thick sections vertical to the myofibril (250–300 g each). Each section was packed into a bag made of high-barrier Nylon film (210 mm×420 mm wide and 0.07 mm thick) in a vacuum and stored for a prescribed period at 2 °C before being used for experiments.

2.4. Measurement of viable counts of total bacteria

Bacteriological samples were obtained by swabbing the meat surface (5 cm×5 cm) with sterilized cotton cloth, followed by homogenizing the cloth with 100 ml of sterile 0.9% saline water. Decimal dilutions were spread over standard agar plates. After incubation for 48 h at 30 °C, colonies on the plates were counted as total viable counts.

3. Results and discussion

3.1. Sensing properties to ethyl acetate

Six sensor elements were tested for their sensitivity to 300 ppm ethyl acetate at temperatures in the range 200–500 °C, as shown in Fig. 3. The sensor fabricated with pure SnO_2 or pure Fe_2O_3 was poorly sensitive to ethyl acetate, with sensitivity values less than 10 over the whole temperature range. The addition of La_2O_3 to In_2O_3 or SnO_2 promoted the sensitivity to 300 ppm ethyl acetate up to about 60 at 300 °C or about 50 at 400 °C, respectively. The addition of Rh to La_2O_3–In_2O_3 further improved the sensitivity up to about 100 at 300 °C, a value about 16 times as high as that of the pure SnO_2 or Fe_2O_3-based sensor. It is suggested that ethyl acetate is oxidized by the absorbed oxygen on the oxide surface. Since ethyl acetate is easily oxidized, poorly

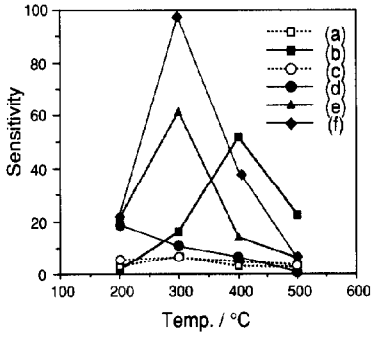

Fig. 3. Sensitivity to 300 ppm ethyl acetate in wet air as a function of temperature. Sensor elements: (a) Sn_2O_3; (b) La_2O_3–Sn_2O_3; (c) Fe_2O_3; (d) La_2O_3–Fe_2O_3; (e) La_2O_3–In_2O_3; (f) Rh–La_2O_3–Sn_2O_3.

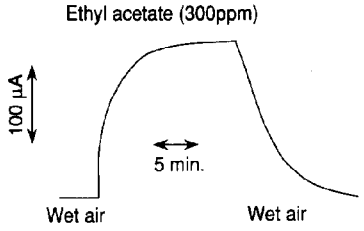

Fig. 4. Response transient of Rh–La_2O_3–In_2O_3 sensor to 300 ppm ethyl acetate at 300 °C.

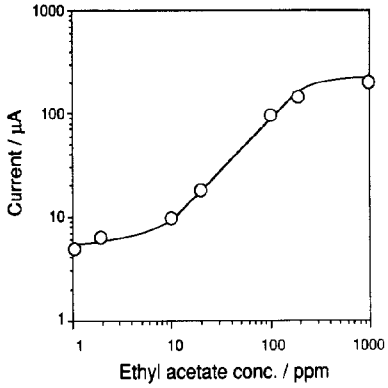

Fig. 5. Dependence of current response of Rh–La_2O_3–In_2O_3 sensor on ethyl acetate concentration at 300 °C.

active oxidation catalysts like Rh and La_2O_3 could promote the gas sensitivity.

Fig. 4 shows the response transient of an Rh–La_2O_3–In_2O_3 sensor at 300 °C on switching on and off 300 ppm ethyl acetate diluted with wet air. On exposure to ethyl acetate, the current response increased rather quickly, achieving 90% of the full change in ≈2 min, and recovered completely to the initial value within ≈8 min when wet air flow was resumed. The current response in the stationary state depended on the concentration of ethyl acetate, as shown in Fig. 5. The calibration curve was linear in the range 10–200 ppm ethyl acetate. As confirmed separately, the same sensor was much less sensitive to ethyl alcohol, acetic acid, and so on at 300 °C. With such sensitivity and selectivity characteristics, this sensor may possibly work as a meat-freshness sensor that monitors the initial bacterial putrefaction of meat on the basis of the concentration of ethyl acetate produced.

3.2. Correlation between gas-sensor method and conventional method

It has been reported that the number of living cells increases up to 10^7 g^{-1} in the initial stage of bacterial putrefaction of meat [6]. In agreement with this, the living cell number in the present study increased slowly up to 10^7 g^{-1} during the initial three days of storage and then increased exponentially. The Rh–La_2O_3–In_2O_3 sensor element was applied to actual beef samples at various stages of bacterial putrefaction to examine its suitability as a meat-freshness sensor. This experiment was carried out by using the sampling system shown in Fig. 6. A portion (10 g) of the stored meat was soaked with water (1 ml) and the resulting meat extract (200 μl) was injected through the sample inlet port of the system onto a filter paper located in a stream of warm air. Volatile components evaporated were introduced into the sensor element chamber through a three-way valve. The sensor responses thus obtained are shown in Fig. 7 as a function of the number of living

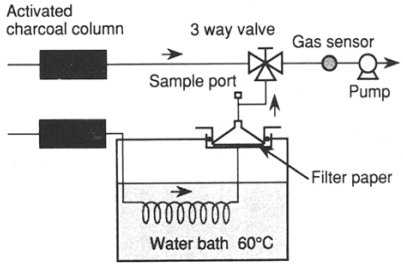

Fig. 6. Sampling system for volatile substances from meat extract.

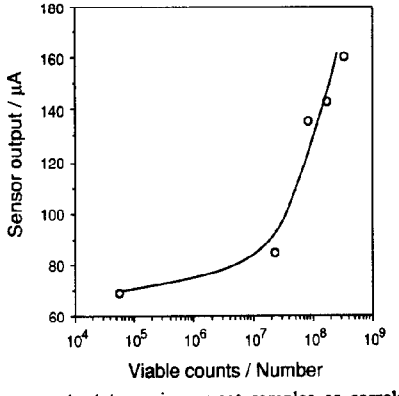

Fig. 7. Sensor output to various meat samples as correlated with the viable counts of the same samples measured with colonies count method (Rh–La_2O_3–In_2O_3 sensor, 300 °C).

cells measured for the same beef samples by using the conventional colony-counting method. It is seen that the sensor response can be correlated with the viable count rather well, particularly in the viable count region exceeding 10^7 g^{-1}. The multiple correlation factor (γ^2) between such a gas-sensor method and the conventional colony counting method was 0.8 for six samples examined. This shows that the present sensor can be applied fairly well for recognizing meat freshness in practice.

4. Conclusions

The La_2O_3–In_2O_3 sensor showed excellent properties of detecting ethyl acetate in wet air at 300 °C. The addition of Rh to La_2O_3–In_2O_3 was effective in improving the ethyl acetate sensitivity. On exposure to volatile components from meat, the Rh–La_2O_3–In_2O_3 sensor produced a response signal which reflected rather well the increase of living cells in the meat during storage, giving rise to a multiple correlation factor of 0.8 to the conventional colony-counting method. Further increase of the sensitivity to ethyl acetate will be useful for improving the accuracy of evaluation of meat freshness.

References

[1] T. Maekawa, Y. Anno, J. Tamaki, N. Miura, N. Yamazoe, Y. Asano and K. Hayashi, Development of semiconductor gas sensor to discern flavors of consomme soup, *Sensors and Actuators B, 13–14* (1993) 713–714.

[2] Y. Anno, T. Maekawa, J. Tamaki, Y. Asano, K. Hayashi, N. Miura and N. Yamazoe, Development of semiconductor gas sensor for 2-methylpyrazine from consomme soup, *Sensors Mater., 5* (1993) 135–142.

[3] M. Fujita, W.T. Jung, H. Tatematsu, D.H. Sohn and T. Maeda, Automated analysis of volatile halogenated hydrocarbons in rain water and ambient air by purge and trap capillary gas chromatography, *J. High Res. Chromatogr., 14* (1991) 83–90.

[4] J. Tamaki, T. Maekawa, S. Matsushima, N. Miura and N. Yamazoe, Ethanol gas sensing properties of Pd–La_2O_3–In_2O_3 thick film element, *Chem. Lett.*, (1990) 477–480.

[5] T. Maekawa, J. Tamaki, N. Miura and N. Yamazoe, Gold-loaded tungsten oxide-sensor for detection of ammonia in air, *Chem. Lett.*, (1992) 639–642.

[6] Y. Yano, N. Kataho, M. Tachibana, T. Nakamura, T. Youdou, J. Miyai, M. Numata and Y. Asano, Monitoring of aging of beef using a meat freshness sensor, *J. Food Ind.*, in press.